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PLUME CHEMISTRY MODELS

SUMMARY OF A PLUME CHEMISTRY WORKSHOP

PHYSICAL DYNAMICS, INCORPORATED

PREPARED FOR

ADVANCED RESEARCH PROJECTS AGENCY

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES

1 APRIL 1973

AFCRL-TR-73-0697

PD-73-036

PLUME CHEMISTRY MODELS

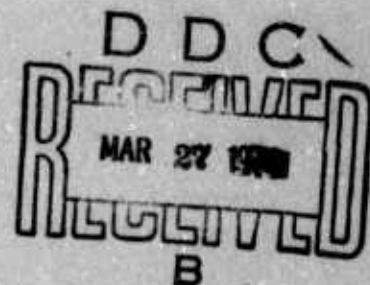SUMMARY OF A PLUME CHEMISTRY WORKSHOP

by

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Contract No. F19628-72-C-0006
Project No. 8692

Scientific Report No. 3

April 1, 1973

Contract Monitor: Alva T. Stair
Optical Physics Laboratory

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Physical Dynamics, Inc. P.O. Box 604, College Park Station Detroit, Michigan 48221	UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

PLUME CHEMISTRY MODELS, SUMMARY OF A PLUME CHEMISTRY WORKSHOP

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Scientific. Interim.

5. AUTHOR(S) *(First name, middle initial, last name)*

Edward R. Fisher

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
April 1, 1973	27	5

8a. CONTRACT OR GRANT NO. ARPA Order No. 1856 F19628-72-C-0006	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 8692	PD 73-036, Scientific Report #3
c. DOD ELEMENT 62301D	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d. DOD SUBELEMENT n/a	AFCRL-TR-73-0697

10. DISTRIBUTION STATEMENT

A - Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
This research was sponsored by the Defense Advanced Research Projects Agency.	Air Force Cambridge Research Labs (OP) L.G. Hanscom Field Bedford, Mass. 01730

13. ABSTRACT

Two plume chemistry models are presented as a result of a workshop meeting in January, 1973. The first model characterizes the chemi-excitation and relaxation processes appropriate to an $O/H/OH/H_2/O_2/H_2O$ system, while the second model characterizes the relaxation processes in a mixture of CO_2, H_2O, H_2, CO, N_2, O and H. These chemistry models are presented for baseline predictions on plume behavior.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Plume Chemistry Models						
Relaxation Model						
APOLLO Model						

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INTRODUCTION

As the plume modeling capabilities continue to
develop under the ARPA Plume Physics Program, a reliable
set of "baseline" chemical mechanisms characterizing
various fuel/atmospheric environments becomes increasingly
important. This importance stems not only from providing
direct comparisons between various flow field calculations
using the same chemical models but also in establishing
a basis upon which to judge improvements in reaction
mechanisms and rate coefficients as new experimental and
theoretical results become available. In this report,
two chemical mechanisms with accompanying rate coefficients
are presented: a chemi-excitation and vibrational relaxation
mechanism for the APOLLO vehicle (H_2/O_2 System), and a gen-
eral vibrational relaxation mechanism for a system consist-
ing of H_2O, CO_2, CO, N_2, O, H and OH species. These reaction
mechanisms are the outgrowth of a chemistry workshop held
at Physical Dynamics, Inc., Berkeley, California on January
12, 1973. A list of attendees to this workshop are given
in Appendix I. It should be noted that the collective in-
put for all attending is represented in these two reaction
mechanisms, particularly with respect to the magnitude of
the proposed rate coefficients.

It will be clear upon reviewing the references accompanying the reaction mechanisms that many rate coefficients are very poorly known particularly for reactions involving atomic and radical species. Experiments underway at Wayne State University, AVCO and CALSPAN under the Plume Physics Program are expected to improve these estimates in the coming months.

In proposing these baseline chemical mechanisms, it should be noted that an attempt was made to include all types of chemical reactions. Thus, reactions with relatively high activation energies generally limited in importance to high temperature regions of the plume are included as well as fast reactions involving reactive intermediates such as OH.

The mechanisms presented in this report should complement the "lumped parameter" hydrocarbon and amine combustion mechanisms recently proposed [Kummler, Fisher, Boynton (1972)] as well as the recent review of vibrational cross section data appropriate to rarified plume environments [Fisher (1972)].

CHEMICAL MODELS

The chemical reactions listed in Table I for the APOLLO system consist of both chemi-excitation and vibrational relacation processes. To date there is no direct information on the rate coefficients for the chemi-excitation reactions [listed as reactions 1) through 18)] except for the overall reactions as reviewed in the Leed's reports [Baulch (1969)]. The rate coefficients for the reactions involving excited states have been estimated following a method of Boynton (1972) which most likely consists of an upper limit to these excited state reactions. The approach taken in these estimates is to assume that vibrational energy in the reactants [e.g., $H_2(v=1)$ as shown in reaction 3)] removes the experimentally observed overall activation energy as compiled in the Leed's reviews. Thus, the high temperature region (above about 1500°K) is dominated by the excited state reaction where $H_2(v=1)$ is present in relatively large concentrations while the low temperature reaction is dominated by the $H_2(v=0)$ reaction. By assuming a Boltzmann population of $H_2(v=1)$ at any given temperature, the additive contribution of reactions 1) and 3) are made to fit the measured overall reaction rate.

The reverse rate coefficients for reactions involving excited states have been calculated from the appropriate equilibrium constant as taken from the Leed's review together with Boltzmann factors to account for the excited state populations. For example, the equilibrium constant for the reaction set

$$O + H_2(v=1) \underset{k_6}{\overset{k_5}{\rightleftharpoons}} OH(v=1) + H$$
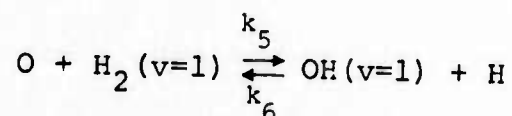
is related to the equilibrium constant for the overall reaction

$$O + H_2 \rightleftharpoons OH + H$$

as given in the Leeds reports by

$$K_{56} = \frac{e^{-E_1/KT}}{e^{-E_2/KT}} \frac{Q_2}{Q_1} K_{Leeds}$$

where E_1 = vibrational spacing of OH

E_2 = vibrational spacing of H_2

Q_1 = vibrational partition function of OH

Q_2 = vibrational partition function of H_2

and K_{Leeds} = thermodynamic equilibrium constant for the overall reaction.

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The reverse rate coefficients for chemical excitation reactions producing H_2O [i.e. reactions 7), 9), 11) and 13)] were calculated from the forward rate coefficients assuming that the H_2O is formed in the vibrational ground state. Note also that the energy transfer reactions [i.e. reactions 14) through 47) and Table II] are only listed in the forward direction. The reverse rate coefficients can be calculated from the Boltzmann factor involving the energy defect (energy available to the translational and rotational modes).

Table III lists the best available Einstein A Coefficients for incorporation into plume chemistry models. Of course the prediction of radiated energy in any given wavelength region depends not only on the total energy available from a given vibrational state as given by the A Coefficient, but also on the spectral shape of that band (i.e. the rotational distribution). A more extensive discussion of this point can be found elsewhere [Boynton, Fisher, Kummler, Thomson (1973)].

TABLE I
APOLLO CHEMISTRY MODEL

	Reaction	Reference	Rate Constant (cc/molecule-sec)
1)	$O + H_2 \rightarrow OH + H$	(a,b)	$1.65^{-13} \exp(-2500/T)$
2)	$H + OH \rightarrow O + H_2$	(c)	$6.9^{-14} \exp(-1425/T)$
3)	$O + H_2(v=1) \rightarrow OH + H$	(d)	$1.3^{-10} \alpha \ (\alpha = 0.9, 0.5)$
4)	$H + OH \rightarrow O + H_2(v=1)$	(c)	$5.5^{-11} \alpha \exp(-4925/T)$
5)	$O + H_2(v=1) \rightarrow OH(v=1) + H$	(d)	$1.3^{-10} (1 - \alpha)$
6)	$H + OH(v=1) \rightarrow O + H_2(v=1)$	(c)	$5.5^{-11} (1 - \alpha) \exp(215/T)$
7)	$OH + H_2 \rightarrow H_2O + H$	(d)	$3.8^{-11} \exp(-2600/T)$
8)	$H + H_2O \rightarrow OH + H_2$	(c)	$1.5^{-10} \exp(-10075/T)$
9)	$OH + H_2(v=1) \rightarrow H_2O + H$	(e)	1.5^{-10}
10)	$H + H_2O \rightarrow OH + H_2(v=1)$	(c)	$5.8^{-10} \exp(-13475/T)$
11)	$OH(v=1) + H_2 \rightarrow H_2O + H$	(e)	1.5^{-11}
12)	$H + H_2O \rightarrow OH(v=1) + H_2$	(c)	$5.8^{-11} \exp(-12475/T)$
13)	$OH + OH \rightarrow H_2O + O$	(a)	$9.6^{-12} \exp(-390/T)$
14)	$O + H_2O \rightarrow OH + OH$	(a)	$9.5^{-11} \exp(-9000/T)$
15)	$O + OH \rightarrow O_2 + H$	(f)	4^{-11}
16)	$H + O_2 \rightarrow O + OH$	(c)	$6.9^{-10} \exp(-8400/T)$
17)	$O + OH(v=1) \rightarrow O_2 + H$	(f)	4^{-11}
18)	$H + O_2 \rightarrow O + OH(v=1)$	(c)	$6.9^{-10} \exp(-13400/T)$

ENERGY TRANSFER REACTIONS*

Vibration-Translation Processes:

19) $H_2(v=1) + H \rightarrow H_2 + H$ (g) $3.2^{-11} \exp(-1400/T)$

20) $H_2(v=1) + O \rightarrow H_2 + O$ (e) $3.0^{-13} \sqrt{T}$

21) $H_2(v=1) + H_2 \rightarrow H_2 + H_2$ (h,i) $1.5^{-7} \exp(-139/T^{1/3})$

22) $H_2(v=1) + H_2O \rightarrow H_2 + H_2O$ (e,j) $1.5^{-7} \exp(-139/T^{1/3})$

23) $N_2(v=1) + H \rightarrow N_2 + H$ (u) $1.9^{-6} \exp(-164/T^{1/3})$

24) $N_2(v=1) + O \rightarrow N_2 + O$ (k,l,m) $1.2^{-13} \exp(-23/T^{1/3})$

25) $N_2(v=1) + H_2 \rightarrow N_2 + H_2$ (n) $3.9^{-8} \exp(-164/T^{1/3})$

26) $N_2(v=1) + H_2O \rightarrow N_2 + H_2O$ (e,j) $3.9^{-8} \exp(-164/T^{1/3})$

27) $OH(v=1) + H \rightarrow OH + H$ (e) 3^{-11}

28) $OH(v=1) + O \rightarrow OH + O$ (e) 3^{-11}

29) $OH(v=1) + H_2 \rightarrow OH + H_2$ (e) 1^{-11}

30) $OH(v=1) + H_2O \rightarrow OH + H_2O$ (e) 3^{-12}

31) $H_2O(010) + H \rightarrow H_2O(000) + H$ (e) 1^{-11}

32) $H_2O(010) + O \rightarrow H_2O(000) + O$ (e) 1^{-11}

33) $H_2O(010) + H_2 \rightarrow H_2O(000) + H_2$ (e,o) 1^{-11}

34) $H_2O(010) + H_2O \rightarrow H_2O(000) + H_2O$ (p) 1^{-11}

35) $H_2O(020) + H \rightarrow H_2O(010) + H$ (t) 2^{-11}

36) $H_2O(020) + O \rightarrow H_2O(010) + O$ (t) 2^{-11}

37) $H_2O(020) + H_2 \rightarrow H_2O(010) + H_2$ (t) 2^{-11}

38) $H_2O(020) + H_2O \rightarrow H_2O(010) + H_2O$ (t) 2^{-11}

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* Note that the reverse rate coefficient can be calculated directly from detailed balance.

39) $H_2O(001) + H \rightarrow H_2O(000) + H$ (e) 1^{-11}

40) $H_2O(001) + O \rightarrow H_2O(000) + O$ (e) 1^{-11}

41) $H_2O(001) + H_2 \rightarrow H_2O(000) + H_2$ (o) 2^{-13}

42) $H_2O(001) + H_2O \rightarrow H_2O(000) + H_2O$ (q) 1^{-12}

43) $H_2O(001) + H \rightarrow H_2O(020) + H$ (e) 1^{-11}

44) $H_2O(001) + O \rightarrow H_2O(020) + O$ (e) 1^{-11}

45) $H_2O(001) + H_2 \rightarrow H_2O(020) + H_2$ (e) 1^{-11}

46) $H_2O(001) + H_2O \rightarrow H_2O(020) + H_2O$ (e) 1^{-11}

Vibration-Vibration Processes

47) $H_2(v=1) + H_2O(000)$

     $\rightarrow H_2(v=0) + H_2O(001)$ (r) $2.5^{-14} T^{5/6} \exp(-30.1/T^{1/3})$

48) $H_2(v=1) + OH(v=0)$

     $\rightarrow H_2(v=0) + OH(v=1)$ (e) 1^{-12}

49) $N_2(v=1) + H_2O(010)$

     $\rightarrow N_2(v=0) + H_2O(001)$ (e) 3^{-13}

50) $N_2(v=1) + H_2O(000)$

     $\rightarrow N_2(v=0) + H_2O(010)$ (s) $9.4^{-11} \exp(-64/T^{1/3})$

51) $H_2O(010) + H_2O(010)$

     $\rightarrow H_2O(020) + H_2O(000)$ (e) $1^{-12} \sqrt{T}$

52) $H_2O(001)$ and $H_2O(100)$ assumed in quasi-equilibrium at the local translational temperature.

8

References (Apollo Model)

a) D.L. Baulch, et. al., High Temperature Reaction Rate Data, Leeds University, (1969).

b) F.P. Boynton, Semi Annual Technical Repart No. 1, Physical Dynamics Report PD-72-020, February(1972).

c) calculated from the forward rate coefficient and detailed balance, using the equilibrium constant as given in the Leeds review [(a) above].

d) estimated from the Leeds review [(a) above] using a method outlined in (b) above.

e) estimate

f) W.E. Wilson Jr., J. Phys. Chem. Refer. Data $\underline{1}$, 535 (1972).

g) R.F. Hiedner and V.V. Casper, Chem. Phys. Letters $\underline{15}$, 179(1972)

h) J.H. Kieffer and R.W. Lutz, J. Chem. Phys. $\underline{44}$, 658(1966) $\underline{45}$, 3888(1966).

i) C. Joffrin, J. Ducuing and J.P. Coffinet, Opt. Commun. $\underline{2}$, 245(1970).

j) past measurements involving water presumably measure both VV and VT processes.

k) W.D. Breshears and P.F. Bird, J. Chem. Phys. $\underline{48}$, 4768 (1968).

l) R.J. McNeal, M.E. Whitson Jr. and G.R. Cook, preprint of work submitted to Chem. Phys. Letters(1972). Aerospace Report SPL 3303, July(1972).

m) D.J. Eckstrom, Stanford Research Institute, unpublished results.

n) D.R. White, J. Chem. Phys. $\underline{46}$, 2016(1967).

o) estimate based on Marriott's cross section values see E.R. Fisher, AFCRL Special Report, 72-0539, August(1972).

p) estimate based on all available data

q) estimate based on analogy to HF VT relaxation

r) estimate based on the modified Rapp model, J. Chem. Phys. <u>40</u>, 573(1964), Fisher unpublished results.

s) estimate based on data of C.W. Von Rosenberg, K.N.C. Bray and N.H. Pratt, J. Chem. Phys. <u>56</u>, 3230(1972) and 13th Symp. (Intern.) on combustion p. 89,(1971).

t) scaled from the analogous rate constant for exciting the lowest bending mode.

u) estimated based on the rate for CO + H; see reference (o) under RELAXATION MODEL (2).

TABLE II

VIBRATIONAL RELAXATION MODEL

Vibration-Translation Processes	Reference	Rate Constant (cc/molecule-sec)
1) $H_2(v=1) + H \rightarrow H_2 + H$	(a)	$3.2^{-11} \exp(-1400/T)$
2) $H_2(v=1) + O \rightarrow H_2 + O$	(b)	$3.0^{-1?} \cdot \sqrt{T}$
3) $H_2(v=1) + H_2 \rightarrow H_2 + H_2$	(c,d)	$1.5^{-7} \exp(-139/T^{1/3})$
4) $H_2(v=1) + H_2O \rightarrow H_2 + H_2O$	(b,e)	$1.5^{-7} \exp(-139/T^{1/3})$
5) $N_2(v=1) + H \rightarrow N_2 + H$	(y)	$1.9^{-6} \exp(-164/T^{1/3})$
6) $N_2(v=1) + O \rightarrow N_2 + O$	(f,g,h)	$1.2^{-13} \exp(-23/T^{1/3})$
7) $N_2(v=1) + H_2 \rightarrow N_2 + H_2$	(i)	$3.9^{-8} \exp(-164/T^{1/3})$
8) $N_2(v=1) + H_2O \rightarrow N_2 + H_2O$	(b,e)	$3.9^{-8} \exp(-164/T^{1/3})$
9) $OH(v=1) + H \rightarrow OH + H$	(b)	3^{-11}
10) $OH(v=1) + O \rightarrow OH + O$	(b)	3^{-11}
11) $OH(v=1) + H_2 \rightarrow OH + H_2$	(b)	1^{-11}
12) $OH(v=1) + H_2O \rightarrow OH + H_2O$	(b)	3^{-12}
13) $H_2O(010) + H \rightarrow H_2O(000) + H$	(b)	1^{-11}
14) $H_2O(010) + O \rightarrow H_2O(000) + O$	(b)	1^{-11}
15) $H_2O(010) + H_2 \rightarrow H_2O(000) + H_2$	(b,j)	1^{-11}
16) $H_2O(010) + H_2O \rightarrow H_2O(000) + H_2O$	(k)	1^{-11}
17) $H_2O(001) + H \rightarrow H_2O(000) + H$	(b)	1^{-11}
18) $H_2O(001) + O \rightarrow H_2O(000) + O$	(b)	1^{-11}
19) $H_2O(001) + H_2 \rightarrow H_2O(000) + H_2$	(j)	2^{-13}
20) $H_2O(001) + H_2O \rightarrow H_2O(000) + H_2O$	(l)	1^{-12}

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21) $H_2O(001) + H \rightarrow H_2O(020) + H$ (b) 1^{-11}

22) $H_2O(001) + O \rightarrow H_2O(020) + O$ (b) 1^{-11}

23) $H_2O(001) + H_2 \rightarrow H_2O(020) + H_2$ (b) 1^{-11}

24) $H_2O(001) + H_2O \rightarrow H_2O(020) + H_2O$ (b) 1^{-11}

25) $CO(v=1) + H \rightarrow CO(v=0) + H$ (o) $5.3^{-7} \exp(-119/T^{1/3})$

26) $CO(v=1) + O \rightarrow CO(v=0) + O$ (p) $1^{-8} \exp(-96/T^{1/3})$

27) $CO(v=1) + H_2 \rightarrow CO(v=0) + H_2$ (q) $9^{-9} \exp(-119/T^{1/3})$

28) $CO(v=1) + H_2O \rightarrow CO(v=0) + H_2O$ (b) $9^{-9} \exp(-119/T^{1/3})$

29) $CO_2(010) + H \rightarrow CO_2(000) + H$ (b) $3.8^{-12} \exp(-7/T^{1/3})$

30) $CO_2(010) + O \rightarrow CO_2(000) + O$ (p) $2.3^{-9} \exp(-77/T^{1/3})$

31) $CO_2(010) + H_2 \rightarrow CO_2(000) + H_2$ (r) $7.6^{-12} \exp(-7/T^{1/3})$

32) $CO_2(010) + H_2O \rightarrow CO_2(000) + H_2O$ (s) 1^{-11}

33) $CO_2(010) + CO_2 \rightarrow CO_2(000) + CO_2$ (r) $4.6^{-10} \exp(-77/T^{1/3})$

34) $CO_2(001) + H \rightarrow CO_2(000) + H$ (t) $6.7^{-8} \exp(-208/T^{1/3})$

35) $CO_2(001) + O \rightarrow CO_2(000) + O$ (t) $1^{-8} \exp(-96/T^{1/3})$

36) $CO_2(001) + H_2 \rightarrow CO_2(000) + H_2$ (t) $9^{-9} \exp(-119/T^{1/3})$

37) $CO_2(001) + H_2O \rightarrow CO_2(000) + H_2O$ (t) $9^{-9} \exp(-119/T^{1/3})$

38) $CO_2(001) + H \rightarrow CO_2(030) + H$ (b) $2.13^{17} T^{-6.34} \exp(-3013/T -378.7/T^{1/3} + 1416/T^{2/3})$

39) $CO_2(001) + O \rightarrow CO_2(030) + O$ (u) $4.6^{24} T^{-5.89} \exp(-4223/T -672.7/T^{1/3} + 2683/T^{2/3})$

40) $CO_2(001) + H_2 \rightarrow CO_2(030) + H_2$ (v) $4.27^{17} T^{-6.34} \exp(-3013/T - 378.7/T^{1/3} + 1416/T^{2/3})$

41) $CO_2(001) + H_2O \rightarrow CO_2(030) + H_2O$ (v) $4.71^{-40}T^{4.54}\exp(2081/T + 454/T^{1/3} - 1729/T^{2/3})$

42) $CO_2(001) + CO_2 \rightarrow CO_2(030) + CO_2$ (v) $9.16^{23}T^{-5.89}\exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$

43) $CO_2(001) + CO \rightarrow CO_2(030) + CO$ (v) $6.87^{23}T^{-5.89}\exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$

44) $CO_2(001) + N_2 \rightarrow CO_2(030) + N_2$ (v) $6.\ell7^{23}T^{-5.89}\exp(-4223/T - 672.7/T^{1/3} + 2683/T^{2/3})$

Vibration-Vibration Processes

45) $H_2(v=1) + H_2O(000)$
$\rightarrow H_2(v=0) + H_2O(001)$ (m) $2.5^{-14}T^{5/6}\exp(-30.1/T^{1/3})$

46) $H_2(v=1) + OH(v=0)$
$\rightarrow H_2(v=0) + OH(v=1)$ (b) 1^{-12}

47) $N_2(v=1) + H_2O(010)$
$\rightarrow N_2(v=0) + H_2O(001)$ (b) 3^{-13}

48) $N_2(v=1) + H_2(000)$
$\rightarrow N_2(v=0) + H_2O(010)$ (n) $9.4^{-11}\exp(-64/T^{1/3})$

49) $H_2O(010) + H_2O(010)$
$\rightarrow H_2O(020) + H_2O(000)$ (b) $1^{-12}\sqrt{T}$

50) $CO_2(001) + H_2O(000)$
$\rightarrow CO_2(010) + H_2O(010)$ (b) 1^{-13}

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51) $N_2(v=1) + CO_2(000)$

$\rightarrow N_2(v=0) + CO_2(001)$ (r) Take the $1.71^{-6}\exp(-175.3/T^{1/3})$
                                             largest
                                             value $6.07^{-14}\exp(15.3/T^{1/3})$

52) $N_2(v=1) + CO(v=0)$

$\rightarrow N_2(v=0) + CO(v=1)$ (v) Take the $1.78^{-6}\exp(-210/T^{1/3})$
                                             largest
                                             value $6.98^{-13}\exp(-25.6/T^{1/3})$

53) $CO_2(001) + CO(v=0)$

$\rightarrow CO_2(000) + CO(v=1)$ (b) $1.56^{-11}\exp(-30.1/T^{1/3})$

54) $CO_2(101) + H_2O(000)$

$\rightarrow CO_2(000) + H_2O(001)$ (b) $2^{-13}\sqrt{T}$

55) $CO_2(021) + H_2O(000)$

$\rightarrow CO_2(000) + H_2O(001)$ (b) $2^{-13}\sqrt{T}$

56) $CO_2(101) + CO_2(000)$

$\rightarrow CO_2(100) + CO_2(001)$ (b) $2^{-11}\sqrt{T}$

57) $CO_2(020) + CO_2(000)$

$\rightarrow CO_2(010) + CO_2(010)$ (b) $4^{-13}\sqrt{T}$

58) $H_2O(020) + H \rightarrow H_2O(010) + H$ (w) 2^{-11}

59) $H_2O(020) + O \rightarrow H_2O(010) + O$ (w) 2^{-11}

60) $H_2O(020) + H_2 \rightarrow H_2O(010) + H_2$ (w) 2^{-11}

61) $H_2O(020) + H_2O \rightarrow H_2O(010) + H_2O$ (w) 2^{-11}

62) $CO_2(020) + H \rightarrow CO_2(010) + H$ (w) $7.6^{-12}\exp(-7/T^{1/3})$

63) $CO_2(020) + O \rightarrow CO_2(010) + O$ (w) $4.6^{-9}\exp(-77/T^{1/3})$

64) $CO_2(020) + H_2 \rightarrow CO_2(010) + H_2$ (w) $1.5^{-11}\exp(-7/T^{1/3})$

65) $CO_2(020) + H_2O \rightarrow CO_2(010) + H_2O$ (w) 2^{-11}

66) $CO_2(020) + CO_2 \rightarrow CO_2(010) + CO_2$ (w) $9.2^{-10} \exp(-77/T^{1/3})$

67) $CO_2(030) + H \rightarrow CO_2(020) + H$ (w) $1.2^{-11} \exp(-7/T^{1/3})$

68) $CO_2(030) + O \rightarrow CO_2(020) + O$ (w) $6.9^{-9} \exp(-77/T^{1/3})$

69) $CO_2(030) + H_2 \rightarrow CO_2(020) + H_2$ (w) $2.3^{-11} \exp(-7/T^{1/3})$

70) $CO_2(030) + H_2O \rightarrow CO_2(020) + H_2O$ (w) 3^{-11}

71) $CO_2(030) + CO_2 \rightarrow CO_2(020) + CO_2$ (w) $1.4^{-9} \exp(-77/T^{1/3})$

72) $H_2O(100)$ and $H_2O(001)$ assumed in quasi-equilibrium at the local translational temeprature.

73) $CO_2(100) + M \rightarrow CO_2(020) + M$ (x)

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(k) estimate based on all available data

(l) estimate based on analogy to HF VT relaxation

(m) estimate based on the modified Rapp model, J. Chem. Phys. 40, 573(1964) Fisher unpublished results.

(n) estimate based on data of C.W. Von Rosenberg, K.N.C. Bray and N.H. Pratt, J. Chem. Phys. 56, 3230(1972) and 13th Symp. (Intern.) on combustion p. 89, (1971).

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(q) W. J. Hocher and R. C. Millikan, J. Chem. Phys. 38, 214 (1963); and R. C. Millikan, J. Chem. Phys. 38, 2855 (1963).

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(t) since direct VT relaxation of $CO_2(\nu_3)$ to ground state has not been unambiguously determined withoug competing VV processes, $CO_2(\nu_3)$ was assumed to relax like $CO(v=1)$.

(u) estimate based on analogy with reaction 35).

(v) estimate based on AVCO suggestion.

(w) scaled from the analogous rate constant for exciting the lowest bending mode.

(x) the Fermi resonance in CO_2 is assumed to couple the (100) and (020) modes with a gas kinetic efficiency independent of collision partner.

(y) estimated based on the rate for $CO + H$, under (o) above.

TABLE III

RADIATIVE LIFETIMES

SPECIES	t(sec)
$OH(v=1)$	0.3
$H_2O(100)$	0.14
$H_2O(010)$	0.045
$H_2O(001)$	0.014
$H_2O(020)$	0.022
$CO_2(010)$	0.33
$CO_2(001)$	0.0025
$CO_2(101)$	0.091

SUMMARY

Two plume chemistry models are presented in this report together with the best available estimate of the rate coefficients. The intent of these models is to provide baseline chemical input to plume flow field calculations to both compare different flow field programs and to provide baseline radiation predictions in an actual plume configuration. As new rate coefficient data becomes available these models will be updated to continue to provide state-of-the-art chemistry mechanisms.

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APPENDIX I

Attendance List to Plume Chemistry Workshop
Held at Physical Dynamics, Inc., Berkeley, California
January 12, 1973

Frederick P. Boynton, Physical Dynamics

Philip E. Cassady, Lockheed-Palo Alto

Paul V. Davis, IDA

Edward R. Fisher, Physical Dynamics (Chairman)

Ralph H. Kummler, Physical Dynamics

Paul F. Lewis, AVCO EVERETT

C. Bradley Moore, University of California-Berkeley

J. Derek Teare, AVCO EVERETT

Kenneth Wilson, Lockheed-Palo Alto

Kurt L. Wray, Boston College

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